

# PATENT SPECIFICATION

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## (54) CATIONIC POLYAMINES AND COMPOSITIONS CONTAINING THEM

(71) We, L'OREAL, a French Body Corporate of 14 Rue Royale, Paris 75008, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In our Specification No. 1416454 we have claimed and described, *inter alia*, cosmetic compositions suitable for application to human hair, which comprise (1) at least one film-forming cationic low molecular weight (defined therein as 1,000 to 15,000) water soluble polymer consisting essentially of recurring units of the formula:



in which A denotes a radical derived from a heterocycle possessing two secondary amino groups, two amine oxide groups or one secondary amino group and one amine oxide group, preferably the



radical, and Z denotes the radical B or B', which radicals may be identical or different and denote a straight-chain or branched-chain alkylene radical, which contains up to 7 carbon atoms in the main chain, is unsubstituted or substituted by one or more hydroxyl groups and which can optionally, contain at least one oxygen nitrogen or sulphur atom and 1 to 3 aromatic and/or heterocyclic rings, the oxygen, nitrogen and/or sulphur atoms being present in the form of ether, thioether, sulfoxide, sulfone, sulphonium, amino, alkylamino, alkenylamino, benzylamino, amine oxide, quaternary ammonium, amido imido, alcohol, ester and/or urethane groups, with

the proviso that Z may not contain more than one ether or thioether linkage, or (2) at least one quaternary ammonium salt of a polymer as defined under (1), in aqueous or aqueous-alcoholic solution.

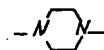
The use of these polymers made it possible to restrict or eliminate the disadvantages resulting from the general condition of the hair, or from sensitising treatments such as bleaching, permanent waving or dyeing.

In our Application No. 32285/75 (Serial No. 1,510,488) we have claimed and described *inter alia*, a composition suitable for application to human hair, which comprises

(1) at least one low molecular weight (as hereinafter defined) cationic film-forming polymer with recurring units of the formula



wherein A denotes



and Z' denotes the radical B<sup>1</sup> or B'<sup>1</sup> which radicals may be the same or different with the proviso that at least one Z' denotes B'<sup>1</sup>; B<sup>1</sup> denotes a straight-chain or branched-chain alkylene radical containing up to 7 carbon atoms in the main chain, and substituted by a hydroxyl group; B'<sup>1</sup> denotes a straight-chain or branched-chain alkylene radical containing up to 7 carbon atoms in the main chain and unsubstituted or substituted by one or more hydroxyl radicals and interrupted by one or more nitrogen atoms, said nitrogen atoms being substituted by an alkyl radical which is optionally interrupted by an oxygen atom and which must contain one or more hydroxyl and/or carboxyl groups; or

(2) a quaternary ammonium salt of a polymer as defined under (1); or

(3) an oxidation product of a polymer as defined under (1), such that at least one of the tertiary amino groups in A is converted to an amine oxide group, together with an acceptable carrier or diluent. These polymers, like those mentioned above, have properties which make them particularly suitable as hair treatment and conditioning agents. In addition to the advantages of conditions, such as improving the combing out of wet hair, the gloss, the softness and the manageability of the hairstyle, the polymers have improved compatibility with surface-active agents usually employed in compositions for the treatment of hair, in particular with anionic surface-active agents.

We have discovered, according to this invention, that cosmetic compositions for hair which contain a polymer with recurring units of formula:



in which A denotes

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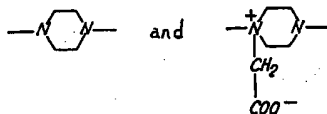


and Z denotes B or B' (as defined hereinabove) can be improved by using the quaternary ammonium salts of these polymers, obtained by quaternisation of, for example, up to 66%, of the basic groups to introduce an acetate group, referred to herein as "betainisation", with for example chloroacetic acid or a chloroacetate, in particular sodium chloroacetate. The yield from the reaction is generally from 60 to 100%. The degree of "betainisation" can be defined as the ratio of the number of equivalents of quaternised nitrogen to the number of equivalents of total quaternisable nitrogen, multiplied by 100. The quaternisation yield of the reaction can be defined as the ratio of the number of equivalents of nitrogen actually quaternised to the number of equivalents of quaternising agent used, multiplied by 100.

We have found that only one of the two tertiary nitrogen atoms of the unit A is easily quaternisable. Betainisation gives units corresponding to the formula



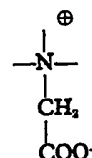
50 in which A' is a mixture of the groups



and Z'' denotes B or B' or a unit obtained by betainisation of B and/or B' if these con-

tain one or more basic nitrogen atoms, which can assume the form

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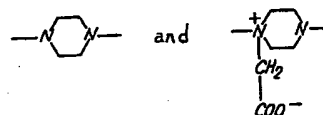
We have found that the compatibility with anionic surface-active agents usually employed in such compositions is improved by quaternising the polymers in this way.

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The present invention thus provides a film-forming cationic, polymer of low molecular weight (as hereinafter defined) with recurring units of the formula



in which A' denotes a mixture of radicals



Z'' denotes B or B' or a unit obtained by betainisation (as hereinbefore defined) of B and/or B', if the latter contains one or more basic nitrogen atoms; and B and B', which may be identical or different, each denotes a straight-chain or branched-chain alkylene radical containing up to 7 carbon atoms in the main chain and is unsubstituted or substituted by one or more hydroxyl groups and is optionally interrupted by at least one oxygen, nitrogen or sulphur atom and 1 to 3 aromatic and/or heterocyclic rings, said oxygen, nitrogen and sulphur atoms being present in the form of ether, thioether, sulfoxide, sulphone, sulphonium, amino, alkylamino, alkenylamino, benzylamino, amine oxide, quaternary ammonium, amido, imido, alcohol, ester and/or urethane groups; as well as compositions suitable for application to human hair comprising these polymers together with a compatible diluent or carrier.

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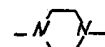
The cationic polymers according to the present application are suitably prepared by "betainisation" (as hereinbefore defined) in aqueous solution of a polymer with recurring units of formula:

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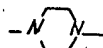
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in which A denotes

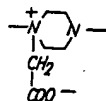


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and Z denotes B or B' (as defined hereinabove) such that at least some of the



radicals are converted to



radicals and, where B and/or B' contain one or more basic nitrogen atoms, at least some of the B and/or B' radicals are "betainised". Suitable methods for preparing the polymer having recurring units of formula



are disclosed in Specification No. 1,416,454.

The polymers of this invention are film-forming and have a relatively "low molecular weight", which is defined herein as not exceeding 15,000 (as determined by the lowering of the vapour pressure). They are soluble in water or in an aqueous-alcoholic medium.

They are particularly effective when used on the hair which has been sensitised as a result of treatments such as bleaching, permanent waving or dyeing, but they can also be used advantageously for normal hair.

These polymers can be introduced, suitably in an amount from 0.1 to 5%, preferably 0.2 to 3%, by weight of the total weight of the composition, into various cosmetic compositions such as lotions, creams or hair-styling gels, as principal constituents, or into shampoos, wave-setting compositions, permanent wave fixing agents and dye compositions, as adjuvants in the presence of other compounds such as anionic, cationic, non-ionic, amphoteric or zwitter-ionic surface-active agents, oxidising agents, synergistic agents, foam stabilisers, sequestering agents, super-fating agents, thickeners, softeners, antiseptics, preservatives, dyestuffs, perfumes and germicides; they can be used as a mixture with other anionic, cationic, amphoteric or non-ionic polymers.

The polymers may be present in the various compositions either in salt form or in the form of free bases, depending on the pH of the compositions which is generally from 3 to 11.

The compositions of this invention are suitably in the form of aqueous, aqueous-alcoholic or alcoholic solutions, of creams, pastes, gels or powders. They can also contain an aerosol propellant and be packaged in an aerosol container.

The hair shampoo compositions according to this invention can contain, in addition to an anionic, cationic, non-ionic, amphoteric and/or

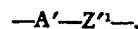
zwitter-ionic surface-active agent and one or more polymers of formula I and/or II, optionally, synergistic agents, foam stabilisers, sequestering agents, super-fating agents, thickeners, cosmetic resins, softeners, dyestuffs, perfumes, bactericides, preservatives and any other adjuvant usually employed in such cosmetic compositions.

The compositions of this invention can also be in the form of, for example, wave-setting lotions, treatment creams, hair conditioners and anti-dandruff lotions.

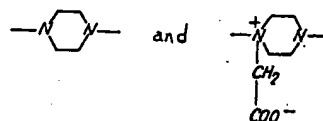
The following Examples further illustrate the present invention. Parts are by weight.

#### EXAMPLE 1

Preparation of a betainised polymer of the type



wherein A' denotes a mixture of radicals



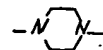
and Z' denotes B, and B denotes



58.25 g (0.51 mol) of sodium monochloroacetate are added to 500 g of an aqueous solution of a polymer of the type



wherein Z denotes B, A denotes

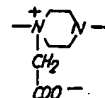


and B denotes



this solution contains 14.2% of active material, has been obtained by condensation, in aqueous solution, of 100 g of piperazine hexahydrate (0.51 mol), 47.7 g of epichlorohydrin (0.51 mol) and 20.2 g of sodium hydroxide (0.51 mol), contains 1 equivalent of quaternisable nitrogen and has a viscosity of 320 cps at 20°C. The mixture is then heated to 90°C for 5 hours. After cooling, the analyses carried out on the solution show a quaternisation yield of 83.4%. The degree of betainisation is 41.7%. The viscosity of the solution after quaternisation is 130 cps.

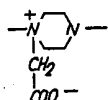
The degree of betainisation of 41.7% indicates that 83.4% of the units A' denote



## EXAMPLE 2

46.7 g (0.4 mol) of sodium monochloroacetate are added to 812 g of the aqueous solution of a cationic polymer, containing 14.2% of active material, described in Example 1, and containing 1.6 equivalents of quaternisable nitrogen, and the mixture is heated to 90°C for 5 hours. The quaternisation yield is 85%. The degree of betainisation is 21%.

In this betainised polymer, 42% of the units A' denote

Application Examples  
EXAMPLE A1

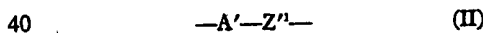
15	Shampoo	
	Compounds of Example 1	2 g
	Sodium lauryl - ether - sulphate polyoxyethyleneated with 2.2 mols of ethylene oxide	12 g
20	Copra ethanolamide	2.5 g
	Carboxymethylcellulose	0.5 g
	Water q.s.p. pH 7.3	100 g

## EXAMPLE A2

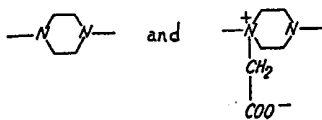
25	Shampoo:	
	Compound of Example 1	1.5 g
	Compound of formula	
	$R \cdot \text{CHOH}-\text{CH}_2\text{O}[\text{CH}_2-\text{CHOH}-\text{CH}_2\text{O}]_{3.5}-\text{H}$	
30	wherein R denotes $\text{C}_6-\text{C}_{12}$ - alkyl	6 g
	Lauryl alcohol polyethoxylated with 12 mols of ethylene oxide	5 g
	Lactic acid q.s.p. pH5	
35	Water q.s.p.	100 g

## WHAT WE CLAIM IS:—

1. A film-forming, cationic, polymer of low molecular weight (as hereinbefore defined) with recurring units of the formula



in which A' denotes a mixture of radicals



Z'' denotes B or B' or a unit obtained by betainisation (as hereinbefore defined) of B and/or B', if the latter contain one or more basic nitrogen atoms; and B and B', which may be identical or different, each denotes a straight-chain or branched-chain alkylene radi-

cal containing up to 7 carbon atoms in the main chain and is unsubstituted or substituted by one or more hydroxyl groups and is optionally interrupted by at least one oxygen, nitrogen or sulphur atom and 1 to 3 aromatic and/or heterocyclic rings, said oxygen, nitrogen and sulphur atoms being present in the form of ether, thioether, sulfoxide, sulphone, sulphonium, amino, alkylamino, alkenylamino, benzylamino, amine oxide, quaternary ammonium, amido, imido, alcohol, ester and/or urethane groups.

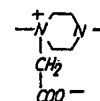
2. A polymer of the formula



in which A denotes



and Z denotes B or B' as defined in claim 1, whenever reacted with a chloroacetate or chloroacetic acid to convert at least some of the A radicals to



and, where B and/or B' contain one or more basic nitrogen atoms, to effect betainisation or at least some of these radicals.

3. A polymer according to claim 1 which is specifically defined in Example 1 or 2.

4. A composition suitable for application to human hair which comprises a polymer as claimed in any one of the preceding claims together with a compatible diluent or carrier.

5. A composition according to claim 4 which is in the form of an aqueous, aqueous-alcoholic or alcoholic solution, a cream, paste, gel or powder.

6. A composition according to claim 4 or 5 which contains from 0.1% to 5% by weight of polymer, relative to the total weight of the composition.

7. A composition according to claim 6, which contains 0.2 to 3% by weight of polymer relative to the total weight of the composition.

8. A composition according to any one of claims 4 to 7 which has a pH from 3 to 11.

9. A composition according to any one of claims 4 to 8 which contains an aerosol propellant.

10. A composition according to any one of claims 4 to 8 which is in the form of a hair shampoo and contains an anionic, cationic, non-ionic, amphoteric and/or zwitter-ionic surface-active agent.

11. A composition according to any one of claims 4 to 10 which contains at least

one thickener, opacifier, sequestering agent,  
super-fattening agent, softener, germicide, pre-  
servative, gum, perfume or dyestuff.

12. A composition according to claim 1  
5 substantially as described in Example A1 or  
A2.

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